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(21) International Application Number: PCT/GB98/00539 (22) International Filing Date: 20 February 1998 (20.02.98) (30) Priority Data: 9704550.4 5 March 1997 (05.03.97) GB (71) Applicant *(for all designated States except US)*: THE SEC-RETARY OF STATE FOR DEFENCE [GB/GB]; Defence Evaluation & Research Agency, Ively Road, Farnborough, Hampshire GU14 0LX (GB). (72) Inventors; and (75) Inventors/Applicants *(for US only)*: SIMPSON, John [GB/GB]; DERA Malvern, St. Andrews Road, Malvern WR14 3PS (GB). BENNETT, Richard [GB/GB]; DERA Malvern, St. Andrews Road, Malvern WR14 3PS (GB). LEWIS, Keith [GB/GB]; DERA Malvern, St. Andrews Road, Malvern WR14 3PS (GB). (74) Agent: SKELTON, Stephen, Richard; D/IPR Formalities Section, MoD Abbey Wood #19, Bristol BS34 8JH (GB).	(81) Designated States: GB, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). **Published** *With international search report.* *Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: DEPOSITION OF THIN FILMS
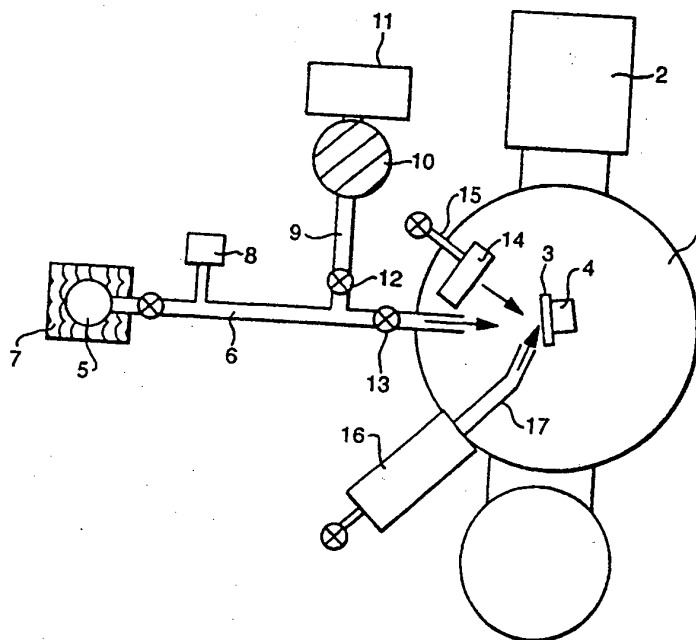
(57) Abstract

Method and apparatus for depositing thin films of materials suitable for use as optical coatings, dielectric insulating layers, bar coatings et al. Chemical precursors of the material to be deposited are transported to a vacuum deposition chamber where deposition place under the action of a chemically reactive species and kinetically energetic species. The optical and other qualities of m produced is shown to depend critically on the ratio of chemically reactive species to chemical precursor.

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Deposition of Thin Films

The current invention relates to the deposition of thin films of material for use in, for example, optical coatings, integrated optical devices or as dielectric insulating layers in electronic devices or as barrier coatings or hard coatings.

Deposition of thin films has been the subject of considerable research effort and various techniques have been developed including vacuum deposition techniques (See for example H A Macleod, "Thin Film Optical Filters", American Elsevier, New York (1969) and chemical vapour deposition (CVD). Vacuum based methods are a standard for the production of optical coatings. The large mean free paths of vapour species under vacuum conditions result in minimal interaction between species in the vapour phase, allowing material to be transported, typically from an evaporation source, across a chamber to condense as a coating on the substrate(s). High uniformity of coating thickness can be achieved by translating the substrate in a rotary or planetary motion across the flux of depositing species. High uniformity, or controlled non-uniformity can also be achieved by the use of appropriately shaped masks placed between the source and substrate. Masks can be used at reduced pressures due to the absence of scattering between vapour species.

The absence of gas phase interaction allows the use of kinetically energetic species such as accelerated ions to bombard the growing coating: the kinetic energy is not diminished by interparticle collision between ion source and substrate. The use of energetic ion or atom bombardment during thin film growth, generally referred to as Ion Assisted Deposition or IAD, has become established as a means of increasing the densification of thin films and allowing greater control of material properties.

In the IAD technique a flux of depositing species is provided by means of thermal evaporation of bulk material, typically by resistance or electron beam heating. The flux of vaporised species condenses on a substrate. The energetic ion beam co-impinges on the substrate. The kinetic energy of the ion beam increases surface adatom mobility and compaction, resulting in high packing densities and refractive indices nearer to bulk values.

In the IAD process the ion flux stimulates surface processes but does not contribute to the flux of depositing species.

Thin film deposition processes using chemical vapour deposition (CVD) have been described by various authors (see for example Pliskin J. Vac Sci Technol Vol 14 No 5 Sept/Oct 1977 and references therein).

CVD processes rely on precursor chemicals such as organometallics, acetylacetonates chlorides, hydrides and metal isopropoxides and derivatives thereof that contain the species to be deposited, usually either an elemental metal or metal containing compound. The precursors can be solid, liquid or gaseous and in the solid or liquid case must be sufficiently volatile to facilitate admittance to the deposition chamber in the vapour phase. The precursor must decompose on heating to give the required element or elements which can then be incorporated into the depositing film.

A drawback of conventional CVD techniques is the need to heat the components to elevated temperature in order to thermally decompose the precursor molecules on arrival at the surface, and then desorb hydrocarbon reaction by-products which would otherwise suppress growth or incorporate in the film, leading to undesirable levels of optical absorption or poor film stability.

The need to heat the components during processing renders CVD processes unsuitable for substrate such as polymers which cannot withstand high temperatures. A number of techniques are well known for the reduction of deposition temperature. Many of these exploit some form of activation in which the substrates are immersed in a plasma discharge. Examples are microwave plasma assisted CVD (eg Greenham et al, Optical Engineering 32 1018 (May 1993) and RF plasma enhanced CVD (eg Kelly et al GB 223 510B). Various authors have reported the deposition of oxides by introducing metal alkoxide precursor directly into an RF discharge (Mukherjee and Evans, Thin Solid Films, 14 (1972) or by introducing metal alkoxide into the downstream of a microwave discharge and most discuss the deposition of SiO_2 using tetraethoxysilane (TEOS).

Pai and Chang (J. Appl. Phys. 68 (2) , July 1990) have reported the deposition of SiO_2 from tetraethoxysilane and N_2O, O_2 and He discharges at substrate temperatures 250-400°C. In this technique the precursor is fed into the deposition chamber and not aimed directly at the substrate. The relatively high chamber pressures used (0.3 - 2.2 mmHg) result in interaction in the gas phase between the radicals and precursor molecules remote from the substrate, resulting in decomposition of TEOS in the chamber volume. Subsequent transport of depositing species to the substrate relies on viscous flow at the high chamber pressures. Wickramanayaka et al (Jpn. J. Appl. Phys. Vol. 33(1994) Pt 1No. 6A) also report deposition of SiO_2 by introducing TEOS into the downstream of microwave and RF plasmas of O_2, N_2, Ar and He at substrate temperatures of 27°C and upwards. Chamber pressures used were 1 to 3.8 mmHg, and reactions in the gas phase and subsequent transport of depositing species by viscous flow to the substrate were dominant growth mechanisms. These authors obtained relatively porous material at room temperature and state that the quantity of deposited film was a function only of the yield of total atomic oxygen for a given substrate temperature, demonstrating that an atomic oxygen:precursor concentration less than unity was being used.

The deposition of titanium dioxide films by atomic oxygen activated CVD under vacuum conditions has been reported (Lewis, Simpson, Pitt and Milward, "Laser Induced Damage in Optical Materials" SPIE 2114, 714-724(1994)). In this example atomic oxygen from a microwave discharge source is piped into the deposition chamber and aimed at the substrate. Deposition is obtained at the substrate and although optical loss free films were produced at sufficient O:precursor ratios, the refractive indices obtained were relatively low (unpublished results) owing to the lack of compaction due to the low kinetic energies of species used.

According to a first aspect of this invention apparatus for deposition of material comprises:

a vacuum deposition chamber;

means for holding a substrate or substrates within the chamber;

at least one source vessel, each of which is for containing a chemical precursor of material to be deposited;

means for the controlled transfer of each precursor from its containing vessel to the deposition chamber;

means for generating within the vacuum chamber at least one type of kinetically energetic species;

means for generating at least one type of chemically reactive species and

means for transferring the chemically reactive species to the deposition chamber and directing same towards the substrate.

The means for generating chemically reactive species might be a saddle field fast atom source or ion source with neutraliser.

In a preferred embodiment the means for transferring the chemically reactive species to the deposition chamber is arranged to avoid direct line of sight between the means for generating the chemically reactive species and the deposition chamber.

The apparatus of may include a plurality of source vessels along with means for closing and opening the vacuum deposition chamber to each of said vessels and means for independently controlling the rates of transfer of chemically active species and, or chemical precursors.

The chemical precursors and/or chemically reactive species may be each transferred to the deposition chamber via flexible tubing which could be directed within the deposition chamber by means of a remotely controlled robot arm.

The means for generating the chemically reactive species comprises a downstream microwave discharge source.

The chemically reactive species might comprise oxygen radicals.

According to a second aspect of the invention a method of depositing metal oxides comprises the steps of

placing a substrate in a deposition chamber;

evacuating said chamber and

directing supply of a chemical precursor of the metal oxide to be deposited and a kinetically energetic non reactive species to the vicinity of the substrate surface.

The metal oxide so produced is substoichiometric. As an option an additional step of directing a supply of chemically reactive oxidising species to the vicinity of the substrate surface may be included in order to produce substantially stoichiometric metal oxide.

In a preferred embodiment the metal oxide is TiO_2, the chemically reactive oxidising species is atomic oxygen and the ratio of atomic oxygen atoms impinging during growth to the number of titanium atoms incorporated in the film is greater than 60. More preferably the ratio is greater than 1400.

Deposition of spatially delineated areas of metal oxide may be achieved by placing a patterned mask in front of the source of kinetically energetic species or by electronic steering of the kinetically energetic species using a robotic arm. Electronic steering of a predominantly ionised beam of energetic species could be achieved using electrodes having controlled voltages applied thereon.

In this application deposition of oxide films in a vacuum system by means of the interaction of metal alkoxide molecules at or near the substrate surface with a beam of kinetically energetic species *or* both a beam of kinetically energetic species and a flux of atomic oxygen radicals is reported. The use of vacuum conditions ensures minimal interaction between species during transport to the substrate, and that the dominant reaction mechanisms are interaction between the various species at or near the substrate surface. The use of vacuum conditions allows preservation of kinetic energy of fast moving species to stimulate surface densification. Unlike the IAD process, where the energetic species promote densification, in this process the inventors show that the kinetically energetic species also promote deposition as well as compaction.

The deposition itself is shown to be a result of interaction of precursor molecules with both the kinetically energetic species and the atomic oxygen. Deposition will occur in the complete absence of atomic oxygen due to the interaction between precursor molecules and the kinetically energetic species alone. Wickramanayaka et al have previously demonstrated deposition from TEOS and excited Ar species in a microwave plasma downstream, but at higher pressures in the gas phase remote from the substrate, rather than under vacuum conditions at the vicinity of the substrate where the benefits of kinetic energy transfer to the growth surface can also be realised.

The process can therefore be run either with only the kinetically energetic species impinging on the substrate, or both kinetically energetic species and also atomic oxygen to provide chemical energy. The observed effect of delivering atomic oxygen to the growth surface is to increase the deposition rate and modify the properties of material deposited.

Importantly, the quantity of atomic oxygen of low kinetic energy but high chemical activity is shown to have a significant effect and both kinetically energetic and chemically energetic species must be present to produce dense material at room temperature. The properties of the material deposited, particularly the optical loss k, the refractive index n, and the stability of the material at elevated temperatures, are shown to be critically dependent on the ratio of atomic oxygen to precursor used.

In particular, the refractive index, as a measure of the density of the material is dependent not only on the densifying effect of the energetic species but also on the quantity of atomic oxygen flux present. For a fixed flux of energetic species, the maximum refractive index obtainable is only reached above a critical atomic oxygen:precursor ratio and the deposition process must be operated in the regime beyond this critical point or optimally dense material will not be produced.

The technique described in this application uses separate sources of high kinetic energy species (argon in the example given) and atomic oxygen radicals. Although these may be combined in to one source of energetic oxygen atoms/ions, keeping the sources separate allows multilayer structures of substoichiometric and stoichiometric oxide to be deposited by simple expedient of constantly running the energetic species source and interrupting the output of the oxygen source.

This invention combines the specific advantages of CVD, namely the high degree of control over growth rate by accurate metering of precursor delivery and the reduction of particulate incorporation due to absence of solid sources in the chamber, with the advantages of vacuum processing such as the use of energetic ions or atoms to promote compaction of the depositing material and the use of masking to control uniformity.

The inventors have demonstrated the deposition in vacuum conditions of substoichiometric metal oxides using the interaction between the precursor and energetic ion beam at the substrate surface rather than in the gas phase remote from the substrate.

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Atomic oxygen radicals can also be introduced to increase the deposition rate and fully oxidise the film to the maximum valence state if required. The properties of the deposited material are governed by both the physical and chemical interaction with kinetically energetic and highly oxidising species.

At suitably high ratios of atomic oxygen:precursor flux, dense, stable films are deposited at room temperature.

In the case of the example provided, semi opaque substoichiometric TiO_x is produced using energetic argon interaction with $Ti(OC_3H_7)_4$. The optical properties of this material when produced under the conditions described are such that the ratio of n/k is in the region of unity. This is the ideal condition required of materials to be used as thin absorbing layers in structures such as the Metal-Dielectric-Metal (MDM) and related types (US 5,279,657). These consist of a back metal reflector, a dielectric spacer and a thin semi opaque metal absorbing top layer. The absorbing top layer enhances chromaticity and is normally made from a grey metal such as Cr.

The use of substoichiometric oxides as absorbing layers in interference structures is addressed in a separate application (UK Appln 9619781.9). Using the invention described, both the dielectric layer and the top absorbing layer of the MDM structure can be deposited using the same apparatus and the same precursor.

In the specific example presented, an energetic argon atom beam is used to decompose metal isopropoxide molecules resident on or close to the substrate surface, resulting in the non-thermal deposition of substoichiometric metal oxides at the chosen surface. However, the process is not limited to the specific example involving the growth of oxides: the method can be applied to other precursor species such as organometallics, which do not themselves contain oxygen, to allow deposition of metals such as Al from precursors such as trimethylaluminium, trimethylaminealane and other such suitable chemicals. Although an electrically neutral beam is preferred , an ion beam may be used and noble gas species other than argon may also be used.

The use of energetic species such as noble gas ions or atoms is restricted to vacuum systems where the mean free path of species is such that the energetic species undergoes a minimum of collisional interactions between source and substrate, allowing the kinetic energy of the species to be preserved until arrival at the substrate vicinity. However, both the precursor and also the atomic oxygen flux can be delivered down tubing which can be made flexible (eg a PTFE lined hose). These flexible delivery tubes can be brought together to form an inlet assembly which could be tracked across a surface by a remotely operated arm. This would enable discrete writing or complex patterning of the film without the need for masking, using substrate wide delivery of energetic species and localised delivery of precursor and oxygen .

In the case of materials which are prone to losing oxygen and darkening under energetic species bombardment, such as TiO_2, decorative coatings featuring semi opaque and transparent areas can be made using substrate wide delivery of both energetic species and precursor and localised delivery of oxygen to produce localised transparent regions.

The invention will now be described, by example, with reference to the following figures in which figure 1 which shows a schematic representation of the apparatus used in a particular embodiment; figure 2 shows the transmission spectra of oxides of titanium grown under different conditions and figure 3 shows the optical loss for a sample of titanium oxide grown by the current invention.

Referring to figure 1, a conventional vacuum chamber 1 is used which is evacuated by a turbomolecular pump 2 which is backed by a rotary pump (not shown). The substrate 3 sits on a holder 4 which is fitted with a heater unit (not shown) and rotation device (not shown) to allow sample heating and rotation if required. Precursor material (in this case titanium isopropoxide) is kept in a stainless steel vessel 5 connected to the deposition chamber 1 via a 1.27cm (0.5") diameter delivery line 6. The vessel 5 is immersed in an oil bath 7 whose temperature determines the vapour pressure above the liquid or solid precursor.

Thus the bath temperature is used to control the rates of precursor transfer in this
embodiment. (Other means such as mass flow controllers or stop valves are also possible).

Although only one precursor vessel is 5 is shown in this embodiment, more than one
precursor vessel 5 may be readily incorporated into the delivery line 6, with suitable means
for switching between them (for example valving off or shuttering). This may be achieved
without the need for modifying the vacuum chamber 1 and would allow more complex
coatings to be deposited, for example ternary or quaternary films such as ferroelectric
barium and lead titanates or superconducting oxides. Multilayer optical stacks are readily
made by switching between precursors and graded refractive index layers may be fabricated
by varying the ratios of precursors as they are simultaneously fed into the chamber.

All surfaces with which the precursor vapour makes contact before entering the deposition
chamber 1 should be sufficiently heated to avoid condensation. Typically, the delivery line 6
is heated to about 20°C above the oil bath temperature

The precursor vapour is measured by a capacitance manometer 8.

Initial setting up can be assisted by inclusion of a vent line 9 running to a cold trap 10 and a
rotary pump 11. By a suitable operation of valve 12, excess vapour can be discharged via the
vent line 9 (for example after opening the precursor vessel 5) in order to achieve the correct
pressure before admission to the deposition chamber 1 via chamber valve 13. The vent line 8
may also be used to evacuate delivery line 6 independently of deposition chamber 1

Additional control of precursor inlet rate to the chamber may be gained by using a low
pressure mass flow controller (not shown). An alternative means of control is to periodically
interrupt the flow of precursor by simultaneously closing chamber valve 13 and opening
vent valve 12. Likewise readmitting precursor is via opening chamber valve 13 and
simultaneously closing vent valve 12. This method avoids pressure transients.

Precursor may be pulsed into the chamber and this operation placed under computer control (not shown), using the capacitance manometer 8 to detect any variation in precursor pressure and modify the pulse mark/space ratio accordingly to maintain a fixed average growth rate.

A flux of kinetically energetic argon atoms is provided by a saddle field fast atom source 14. The source consists of a stainless steel box lined with carbon plates (not shown) with a carbon rod positioned centrally within the source (not shown) and attached to the high voltage feed (not shown). Feed gas enters the unit via a capillary inlet tube 15. Discharge takes place within the unit, between the central anode rod (not shown) and front and rear carbon wall linings (not shown) which act as cathodes. The front cathode is perforated to allow exit of energetic species. The high recombination rates within the plasma produce a beam with a high percentage of neutral species. The source is positioned such that the front grid is aimed at the substrate. Typical pressures within the source are 10^{-3} mbar and operation is at 1-2 kV. Rate of admission of argon may be controlled by needle valve or mass flow controller (not shown).

An atomic oxygen flux is provided by a downstream microwave discharge source 16 (see GB 9009319). Discharge takes place within a 2.54 cm (1") diameter silica tube (not shown). The silica tube, which also acts as a vacuum envelope, sits within a standard Evenson microwave cavity (external to the vacuum). Toroidal confining magnets (not shown) are fitted outside the tube. A 2.45 GHz RF frequency signal is transmitted via coaxial cable (not shown). A baffle plate (not shown) situated downstream of the discharge region maintains the tube at operating pressure whilst preserving vacuum conditions within the deposition chamber 1. Oxygen radicals escape via an aperture in the middle of the plate.

The atomic oxygen flux is transported via a delivery tube 17 to impinge on the substrate 3. One or more bends are incorporated in the tube 17 to prevent charged species from the discharge tube reaching the substrate. The delivery tube should be constructed of, or lined with, materials that have low atomic oxygen recombination coefficients, for example borosilicate glass B_2O_3 or PTFE.

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Any discharge source which produces atomic oxygen could in principle be used, for example 13.56 MHz RF sources, Electron Cyclotron Resonance sources. or dc glow discharge. However the means of producing atomic oxygen must have a high conversion efficiency. It is important to keep the overall gas flow into the chamber as low as possible, to allow high atomic oxygen radical fluxes to be delivered to the substrate whilst maintaining pressures of 10-3mbar or less within the deposition chamber. Pressures of this level or lower are necessary to minimise interaction between species in the gas phase and confine reactions to the vicinity of the substrate.

Growth occurs where the precursor and flux of energetic species co-impinge on the substrate. The example cited here is for the growth of substoichiometric TiO_2 (also referred to as TiO_x) using titanium isopropoxide $Ti(OC_3H_7)$ as the precursor.

Typical conditions used are a bath temperature of 40°C, giving gas line precursor partial pressures of the order $10Nm^{-2}$ (0.1mbar). Typical discharge conditions in the FAB gun are 1.9 KeV, 18 mA and argon feed of 10 sccm. Using these conditions, with the substrate at near ambient temperature and typical deposition chamber pressures of $10^{-2}Nm^{-2}$ gives growth rates of the order 0.1×10^{-2} m per hour.

Transmission spectrum of material grown under these conditions is shown in figure 2a. Material grown under these conditions exhibits high optical loss levels typical of substoichiometric TiO_x. Demonstration that this is primarily a surface reaction has been shown by masking off a section of the argon beam such that only a isolated area of substrate is exposed to the energetic argon flux, whilst projecting the precursor flux over the entire substrate area. A well defined localised area of deposit is produced under these conditions.

Keeping the above conditions fixed, and introducing an atomic oxygen flux, an increase in growth rate is obtained, together with a decrease in optical loss and an increase in refractive index. The quantities of atomic oxygen used are described here in terms of the total number of the number of oxygen atoms delivered to a unit area in a given time ratiod to the total number of titanium atoms incorporated in a unit area of the film deposited within that time.

TiO$_2$ films with minimal or no optical loss, k, in the visible are obtained at an approximate ratio of 60:1 atomic oxygen: titanium (figure 3). At and below the approximate ratio of 140:1, inhomogeneous films are produced, evidenced in transmission spectra by half wave fringe maxima lying above the transmission level of the bare substrate. Above this level, no evidence for this inhomogeneity is observed. Up to O:Ti ratios of approximately 1400:1, the refractive index continually increases, reaching 2.27 at 500nm (figure 4). A transmission spectrum of TiO$_2$ grown under these conditions is shown in figure 2b. The ratios referred to are obtained by measuring the atomic oxygen flux using the technique described in Satchell (Supercond. Sci. Technol. Vol. 6 (1993)379-380). The number of metal atoms in a unit area of the deposited layer is then calculated. The O:Ti ratio (in the case of titanium oxide) is then obtained by dividing the total oxygen radical flux arriving at the surface during time of growth by the number of metal atoms incorporated in the layer.

On heating deposited films to 200°C, some exhibit a darkening due to an increase in optical loss. On leaving at room temperature for some time this darkening decreases, indicating that it is due to water or OH groups being driven from and subsequently re-entering the material. This is not hydrogen bonded water within pores as the presence or otherwise of free water would not result in darkening, and instead appears to be linked to hydroxyl groups incorporated on the lattice instead of oxygen. At or above an atomic O:Ti ratio of 1400:1, the deposited film is resistant to darkening on heating to 200°c for 60 minutes or more.

Atomic force microscopy of TiO$_2$ films deposited using this technique shows these films to be extremely smooth, with surface roughness of 0.2 nm rms and free of pores and inclusions. The extreme smoothness and defect free nature of films deposited by this method makes it attractive for applications where stability and low scatter levels are needed.

Deposition of substoichiometric Al$_2$O$_3$ and SiO$_2$ using aluminium isopropoxide Al(OC$_3$H$_7$)$_3$ and tetraethylorthosilicate Si(OC$_2$H$_5$)$_4$ has under similar conditions been demonstrated by the authors.

As discussed in Lewis, Simpson, Pitt and Milward, "Laser Induced Damage in Optical Materials" SPIE 2114, 714-724 (1994), TiO_2 can be produced by precursor and atomic oxygen coimpinging in a vacuum system, and the authors have subsequently demonstrated a similar result for Al_2O_3. However in the case of SiO_2 from TEOS, deposition is not observed using a flux of precursor and atomic oxygen alone and is only obtained with either the beam of kinetically energetic species interacting with the precursor or the kinetically energetic species and atomic oxygen radical flux coimpinging. This unexpected result demonstrates that for the case of SiO_2 films prepared using this invention, the growth process is not comparable with that reported by other authors at higher pressures where deposition can be obtained by interacting TEOS with oxygen radicals.

HfO_2 is a valued high index material for ultra violet applications. The authors have demonstrated deposition from Hf-t-butoxide $Hf(OC_4H_9)_4$ using interaction with kinetically energetic argon alone, interaction with precursor and atomic oxygen radical alone and precursor with both kinetically energetic argon and atomic oxygen impinging together.

Deposition of hafnium oxide is obtained using interaction with kinetically energetic argon. Figure 3 a shows the transmission spectrum for hafnium oxide grown under these conditions. The refractive index is relatively high (1.94 at 500 nm). Optical loss is zero at 600nm wavelength but increases moving to shorter wavelength, showing material is substoichiometric.

Introducing a low atomic oxygen radical flux results in a large increase in growth rate, but a decrease in refractive index and a large level of optical loss across the visible waveband, particularly high in the ultraviolet wavelength region around 300nm (figure 3b). This demonstrates incomplete reaction of the precursor and considerable hydrocarbon incorporation. An atomic oxygen to incorporated Hf atom (O:Hf) ratio of <10:1 was used. As the atomic oxygen flux level is increased, the refractive index rises and the optical loss level decreases, as reaction of the precursor to the pure oxide becomes more complete.

Figure 3C shows transmission spectrum of high quality high quality material produced by coimpingement at the substrate of precursor, kinetically energetic argon and atomic oxygen. An O:Hf ratio of approximately 800:1 was used.

Table 1 shows a summary of optical properties of HfO_2 films grown using precursor and energetic argon, and precursor, argon and oxygen radical flux.

Table 1.

Conditions	O:Hf	n 280nm	k 280nm	n500nm	k500nm
Ar only,noO	----	2.11	0.012	1.94	0.002
Ar + O	<1	1.75	0.046	1.71	0.005
Ar + O	10	2.14	0.008	2.00	0.0002
Ar + O	385	2.14	0.005	1.985	0.0002
Ar + O	774	2.145	0.0015	2.00	0.0000
Ar + O	1950	2.145	0.0015	2.00	0.0000

CLAIMS

1. Apparatus for deposition of material comprising:

a vacuum deposition chamber;

means for holding a substrate or substrates within the chamber;

at least one source vessel, each of which is for containing a chemical precursor of material to be deposited;

means for the controlled transfer of each precursor from its containing vessel to the deposition chamber;

means for generating at least one type of kinetically energetic species and for directing the kinetically energetic species towards the vicinity of the substrate;

means for generating at least one type of chemically reactive species; and

means for transferring the chemically reactive species to the deposition chamber and directing same towards the vicinity of the substrate;

2. The apparatus of claim 1 where the means for generating at least one type of chemically reactive species is a saddle field fast atom source.

3. The apparatus of claim 1 where the means for generating at least one type of chemically reactive species is an ion source with neutraliser.

4. The apparatus of claim 1 where the means for transferring the chemically reactive species to the deposition chamber is arranged to avoid direct line of sight between the means for generating the chemically reactive species and the substrate.

5. The apparatus claim 1 and further including a plurality of source vessels along with means for closing and opening the vacuum deposition chamber to each of said vessels.

6. The apparatus of claim 1 and further including means for independently controlling the rates of transfer of chemically active species and chemical precursors.

7. The apparatus of claim 1 and further including means for directing the chemical precursors as they enter the deposition chamber

8. The apparatus of claim 1 and further including means for directing the chemically reactive species as they enter the chamber

9. The apparatus of claim 1 where the chemical precursors and/or chemically reactive species are each transferred to the deposition chamber via flexible tubing which is directed within the deposition chamber by means of a remotely controlled robot arm.

10. The apparatus of claim 1 where the means for generating the chemically reactive species comprises a downstream microwave discharge source.

11. The apparatus of claim 1 where the chemically reactive species comprises an oxidising species.

12. The apparatus of claim 11 where the oxidising species comprises oxygen radicals.

13. The apparatus of claim 1 where the means for generating kinetically energetic species is separated from the means for generating chemically reactive species so that interaction between the reactive species and the kinetically energetic species occurs only in the vicinity of the substrate.

14. The apparatus of claim 1 and further including evacuating means for evacuating said deposition chamber to a pressure $\leq 10^{-3}$ mbar.

15. The apparatus of claim 1 where the means for generating the kinetically energetic species is sufficiently remote from the substrate that the temperature of the substrate is substantially at room temperature during the generation of the kinetically energetic species.

16. Apparatus for deposition of material comprising:

a vacuum deposition chamber;

means for evacuating said deposition chamber to a pressure $\leq 10^{-3}$ mbar;

means for holding a substrate or substrates within the chamber;

at least one source vessel, each of which is for containing a chemical precursor of material to be deposited;

means for the controlled transfer of each precursor from its containing vessel to the deposition chamber;

means for generating at least one type of kinetically energetic species and for directing the kinetically energetic species towards the vicinity of the substrate.

17. The apparatus of claim 16 where the means for generating the kinetically energetic species is sufficiently remote from the substrate that the temperature of the substrate is substantially at room temperature during the generation of the kinetically energetic species.

18. The apparatus of claim 16 where the means for generating at least one type of kinetically energetic species is a saddle field fast atom source.

19. A method of depositing a material comprising the steps of

placing a substrate in a deposition chamber;

evacuating said chamber to a pressure $\leq 10^{-3}$ mbar and

directing supply of a chemical precursor of the material to be deposited and a
kinetically energetic species to the vicinity of the substrate surface.

20. The method of claim 19 and further including the steps of generating a chemically
reactive species and directing the chemically reactive species to the vicinity of the substrate
surface.

21. The method of claim 20 where the oxide is TiO_2 and the chemically reactive species is
atomic oxygen, wherein that the ratio of atomic oxygen atoms impinging during growth to
the number of titanium atoms incorporated in the film is greater than 60.

22. The method of claim 21 characterised in that the ratio of atomic oxygen atoms
impinging during growth to the number of titanium atoms incorporated in the film is greater
than 1400.

23. A method as claimed in claim 19 further including the step of placing a patterned mask
in front of the source of kinetically energetic species to achieve deposition of spatially
delineated areas of metal oxide.

24. A method as claimed in claim 19 whereby deposition of spatially delineated areas of
metal oxide is achieved by electronic steering of the kinetically energetic species using a
robotic arm.

25. A method as claimed in claim 19 whereby deposition of spatially delineated areas of oxide is achieved by electronic steering of a predominantly ionised beam of kinetically energetic species using voltages applied to electrodes to deflect the beam.

26. A method as claimed in claim 19 characterised in that the oxide is SiO_2 and the chemical precursor is tetraethylorthosilicate TEOS.

27. A method of claim 20 where the method for directing the chemically reactive species to the substrate avoids a direct line of sight between the means for generating the chemically reactive species and the substrate.

28. A method of claim 20 where the generation of the kinetically energetic species is separated from the generation of the chemically reactive species so that interaction between the reactive species and the kinetically energetic species occurs only in the vicinity of the substrate.

29. A method of claim 19 where the generation of the kinetically energetic species is sufficiently remote from the substrate that the temperature of the substrate is substantially at room temperature during the generation of the kinetically energetic species.

Fig.1.
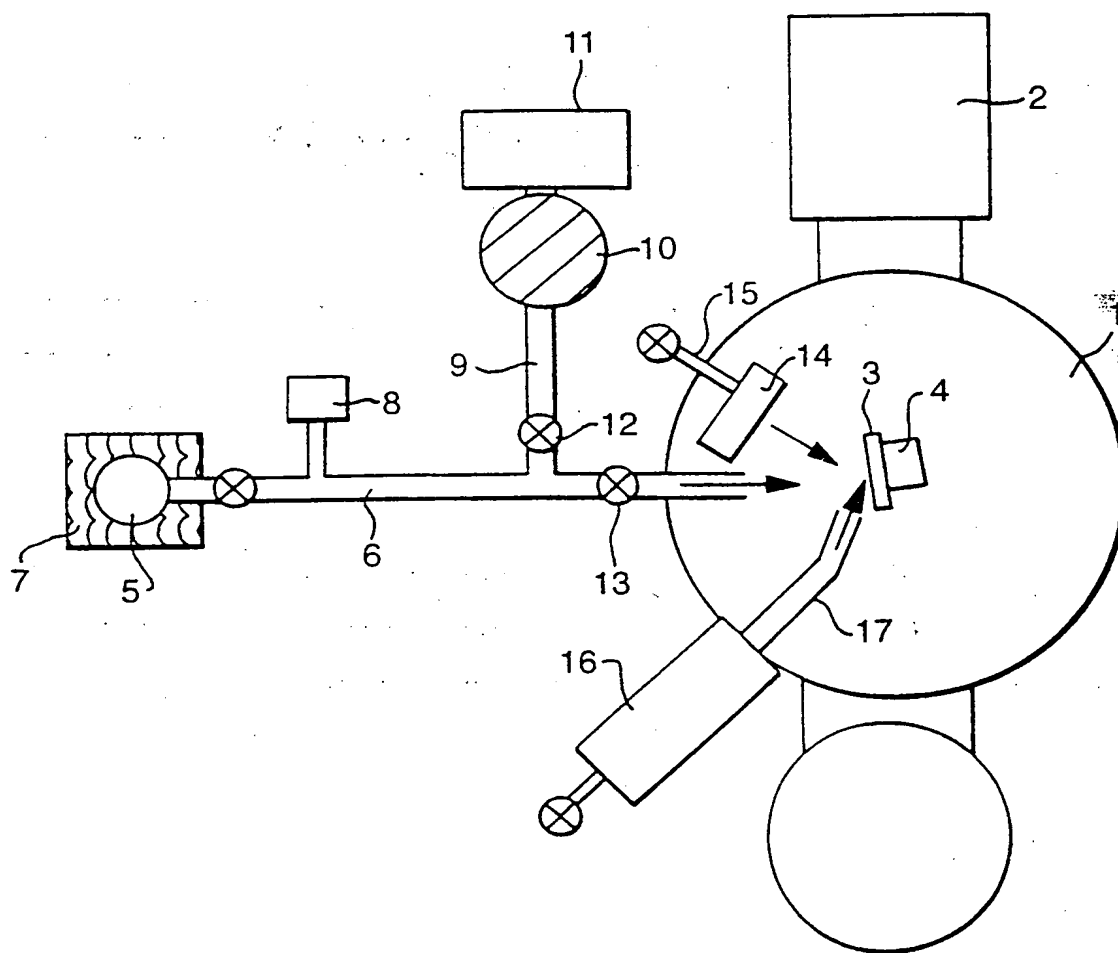
Fig.2.
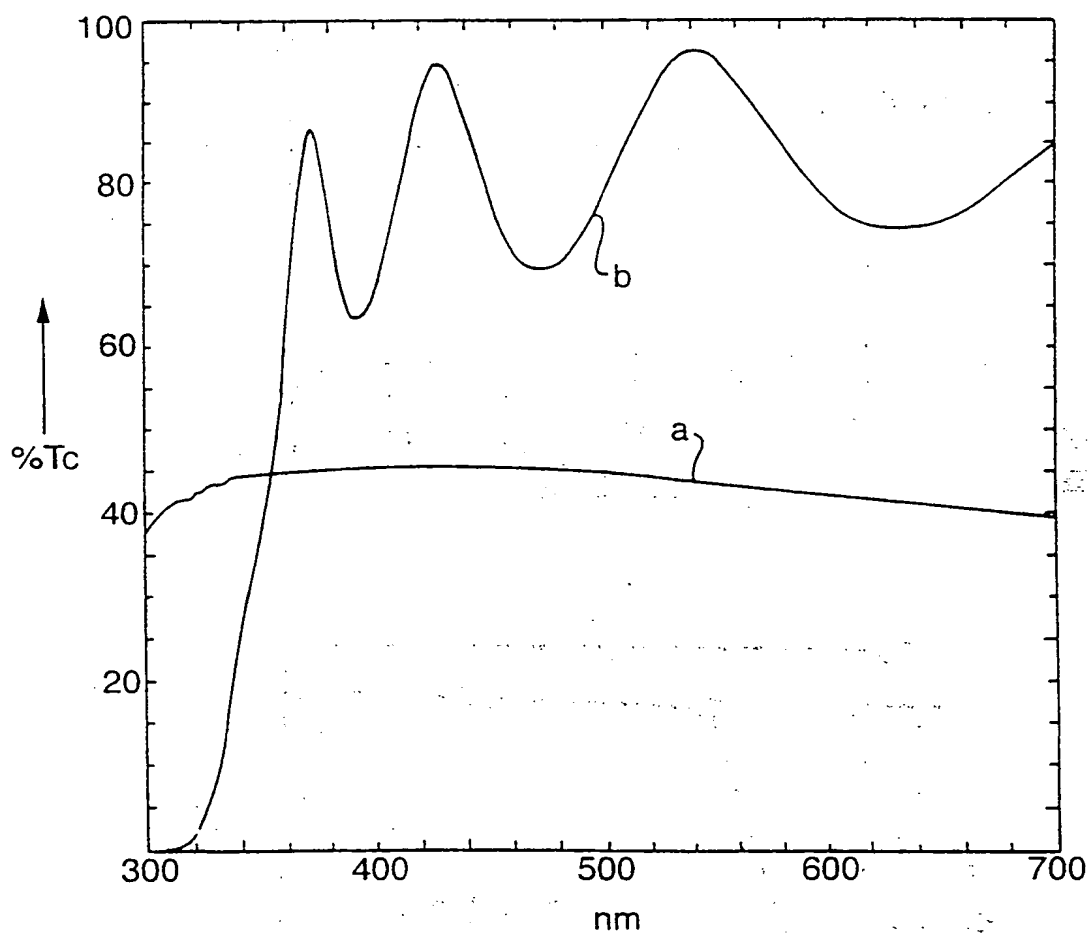
Fig.3.
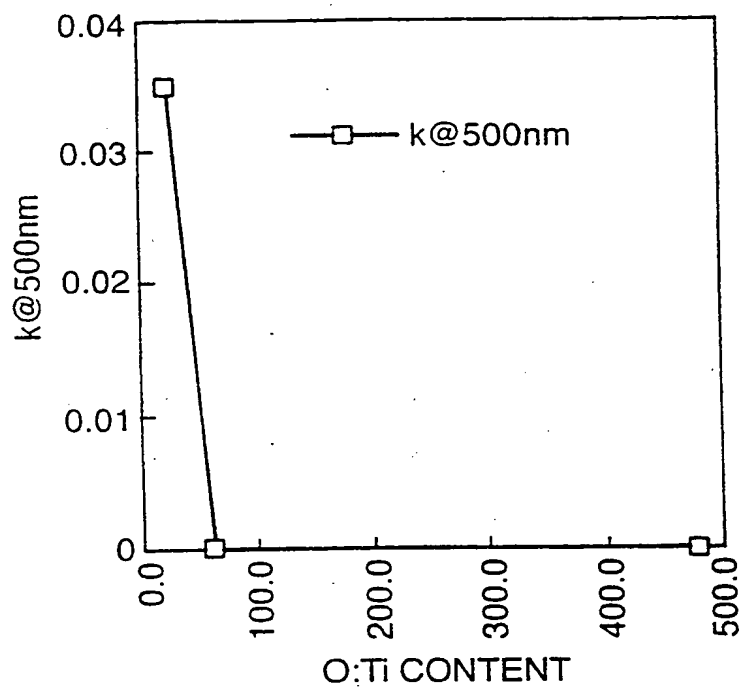
Fig.4.
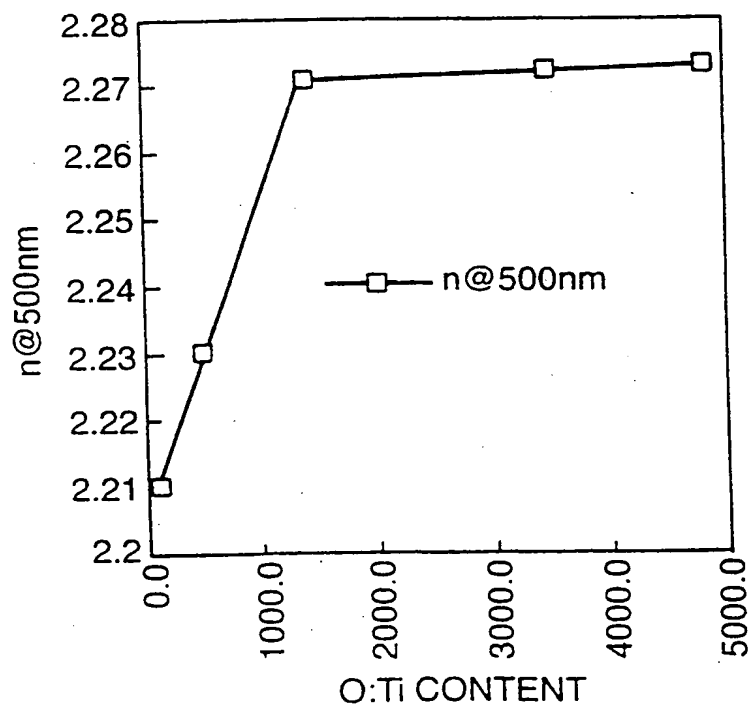
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6   C23C16/48   C23C16/44   C23C16/04   C23C16/40

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   C23C

Documentation searched other than minimumdocumentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 083 033 A (KOMANO HARUKI ET AL) 21 January 1992	1,5-8, 10-14, 16,19, 20,26,28
Y	see column 5, line 48 – column 7, line 38; figures 8,11	4,9,24, 25,27
X	US 4 599 135 A (TSUNEKAWA SUKEYOSHI ET AL) 8 July 1986 see column 2, line 56 – column 4, line 14; claim 6	1,3, 15-19,29

-/--

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publicationdate of another citation or other special reason (as specified)

"O" document referring to an oral disclosure. use. exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of theinternational search	Date of mailing of the international search report
18 June 1998	03/07/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Ekhult, H

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
Y	LENSKI M ET AL: "SUBSTRATE TEMPERATURE DEPENDENT PHOTOELECTRICAL AND STRUCTURAL PROPERTIES OF A-SI:H DEPOSITED BY HYDROGEN ASSISTED CHEMICAL VAPOURDEPOSITION" THIN SOLID FILMS, vol. 288, no. 1/02., 15 November 1996, pages 337-345, XP000691307 see figure 1 ---	4,27
Y	WO 96 00803 A (FEI COMPANY) 11 January 1996 see claims 1-3 ---	24,25
Y	US 4 803 947 A (UEKI MASAO ET AL) 14 February 1989 see column 18, line 16 - line 42 ---	9
A	SCHEUER V ET AL: "ELECTRON BEAM DECOMPOSITION OF CARBONYLS ON SILICON" MICROELECTRONIC ENGINEERING, vol. 5, no. 1 - 4, + INDEX, December 1986, pages 423-430, XP000039652 see figure 1 ---	23
A	LEINEN D ET AL: "ION BEAM INDUCED CHEMICAL VAPOR DEPOSITION FOR THE PREPARATION OF THIN FILMS OXIDES" THIN SOLID FILMS, vol. 241, no. 1/02, 1 April 1994, pages 198-201, XP000440450 see paragraph 2-3 ---	21,22
A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 095 (E-395), 12 April 1986 & JP 60 236233 A (KOGYO GIJUTSUIN;OTHERS: OJ), 25 November 1985, see abstract ---	1-29
A	COOPER C V ET AL: "The effect of TiN interlayers on the indentation behavior of diamond-like carbon films on alloy and compound substrates" SURFACE AND COATINGS TECHNOLOGY, MARCH 1994, SWITZERLAND, vol. 63, no. 3, ISSN 0257-8972, pages 129-134, XP002068527 see paragraph 2 ------	2

INTERNATIONAL SEARCH REPORT

Information on patent family members

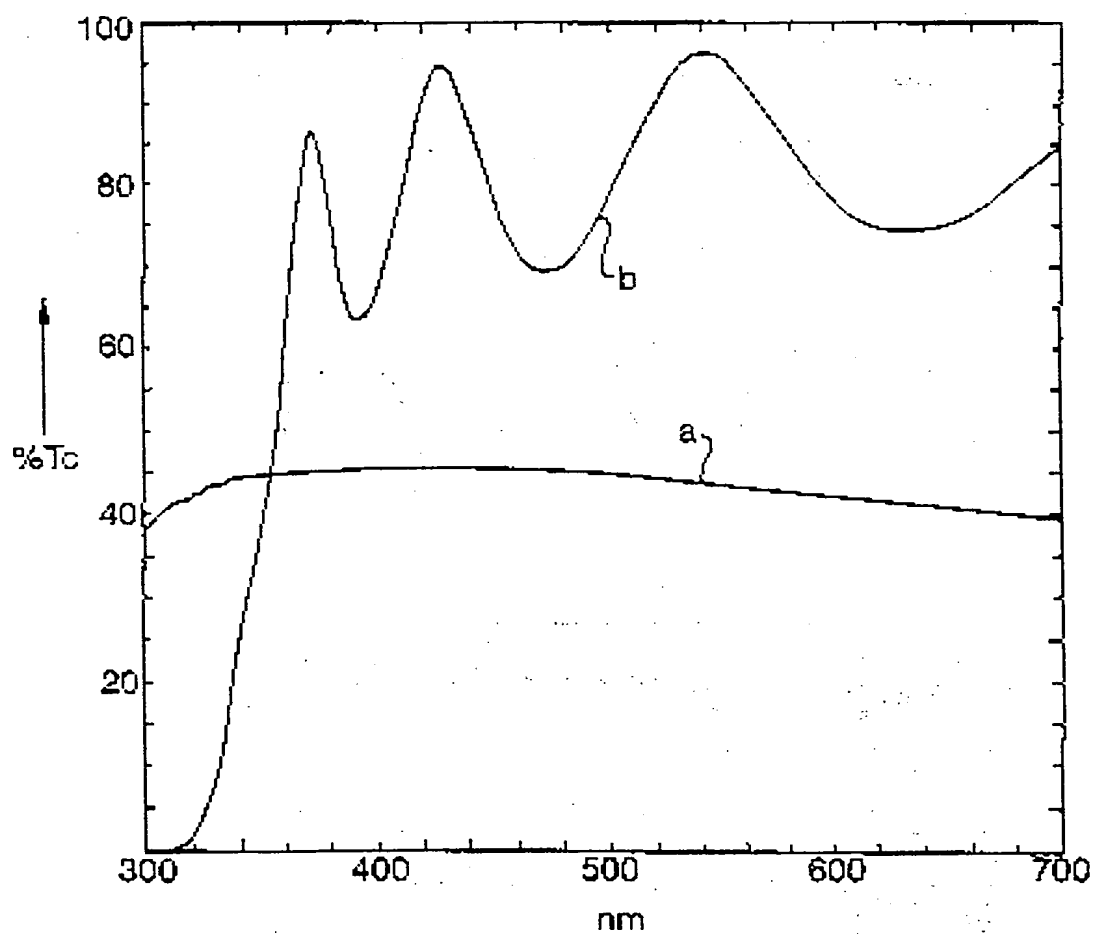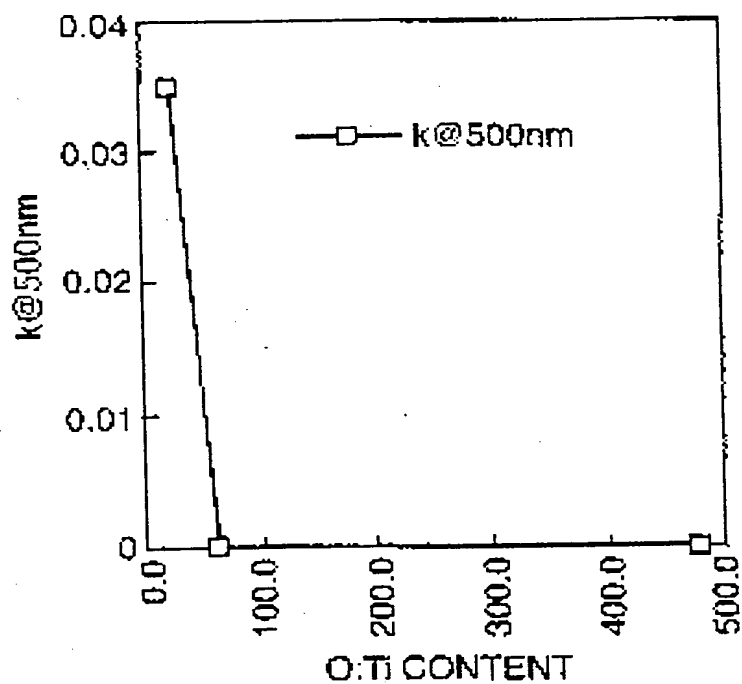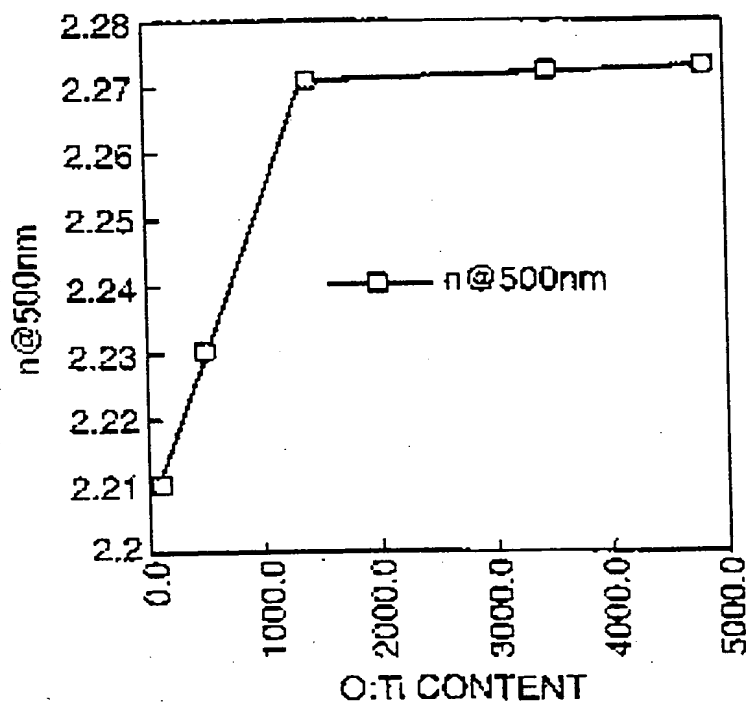| Patent document cited in search report		Publication date	Patent family member(s)		Publication date
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			JP	3016127 A	24-01-1991
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Fig.1.
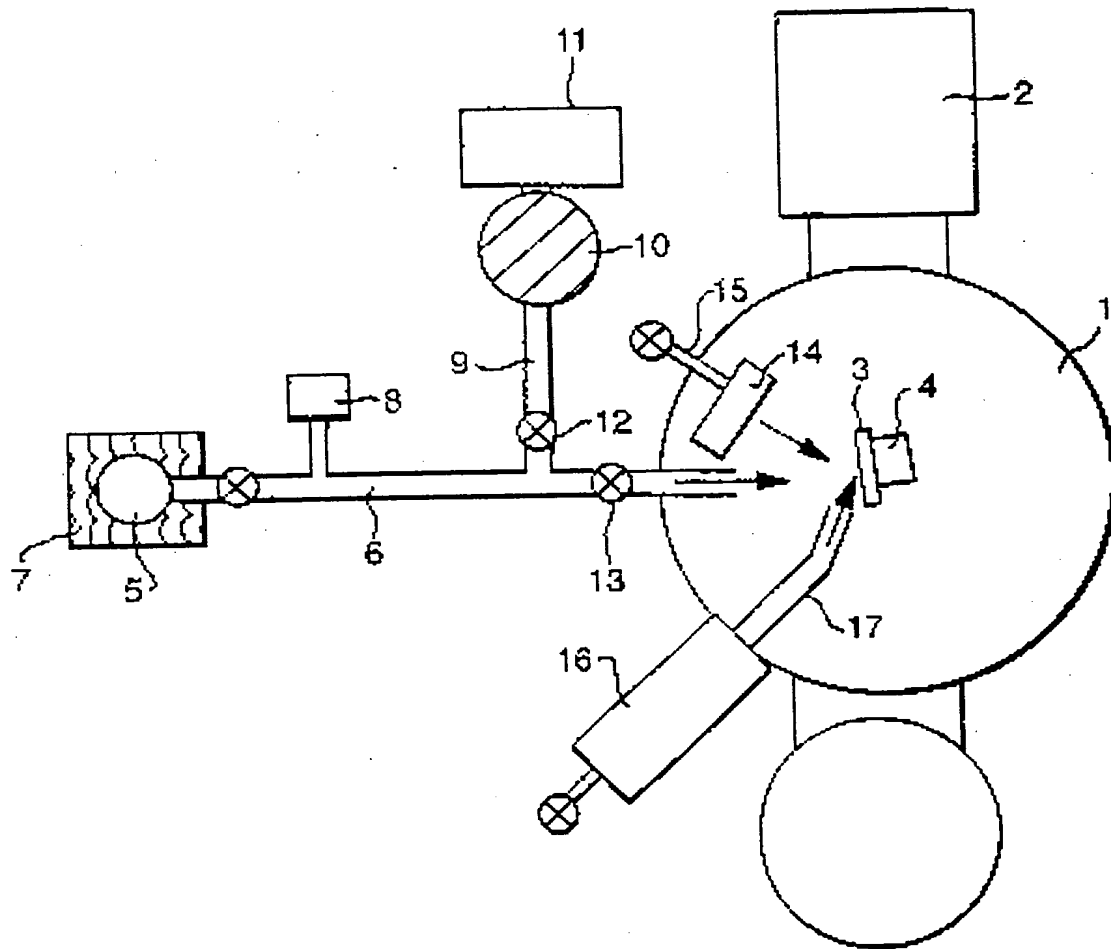
Fig.2.

Fig.3.

Fig.4.

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